Di(cyclopentadienyl)zirconium(II) Bis(phosphine) Complexes

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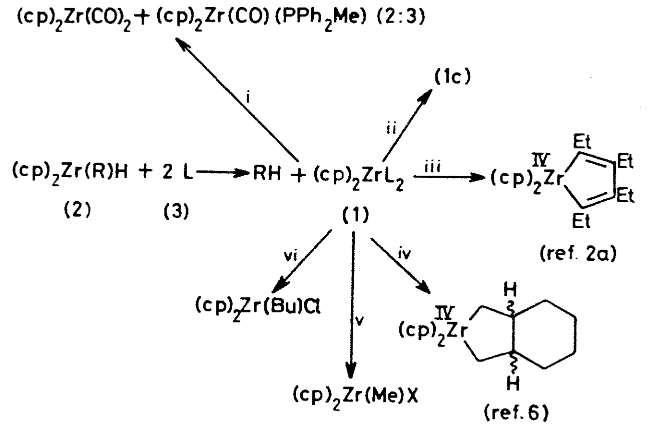
Summary Reactive di(cyclopentadienyl)zirconium(II) bis(phosphine) complexes were prepared by phosphine ligand-induced reductive elimination from $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(H)R]$, R = alkyl.

LOW-VALENT metallocenes of the early transition metals display unusual structural patterns and great reactivity, which has hampered their synthesis. For example, preparation of Group 4 metallocenes, by alkali metal reduction of the corresponding metallocene dichloride, has rarely led to the desired compound. Under these conditions, the reduced species usually deactivates to give complexes of the metal in a higher oxidation state, producing dimers, polymers, or species incorporating exogenous ligands.[1] We recently noted[2] that various ligands induce reductive elimination of an alkane from di(cyclopentadienyl)-zirconium ('zirconocene') alkyl hydrides,[3] (**2**), ultimately producing Zr^{IV} complexes derived from a precursor Zr^{II} metallocene. By ligand-induced reductive elimination we have prepared highly reactive Zr^{II} bis(phosphine) complexes (**1**) through reaction of (**2**) with tertiary phosphines. In this synthesis, hydrocarbon is the sole byproduct. These zirconium complexes are an efficient source of monomeric '$(Cp)_2Zr$.'

A cold toluene solution (−20 °C) or cyclohexane suspension (6 °C) of (**2**) was treated with a tertiary phosphine (3 equiv.)† and the initially colourless solution rapidly darkened. When the mixture was warmed to room temperature, a quantitative yield (by n.m.r. spectroscopy) of $(Cp)_2ZrL_2$ (L = monophosphine) (**1**) and methylcyclohexane was obtained‡ (Scheme 1). Compound (**1d**) is stable at room temperature and has been isolated as air- and moisture-sensitive black-green crystals§ [^1H(δ C_6D_6): 4·80 (t, J_{P-H} 1·5 Hz, 10H), 1·00 (m, 12H), and 0·69 (m, 4H); $^{13}C\{^1H\}$ (δ C_6D_6): 88·66, 33·78, and 18·70 p.p.m.; $^{31}P\{^1H\}$ (δ *vs.* H_3PO_4, C_6D_6): 60·9 p.p.m.]. The bis(phosphine) complexes (**1a, b**) of simple monophosphines are not isolable, but they have spectral properties analogous to those of (**1d**). They are used *in situ* and are moderately stable at room temperature in solution in the presence of excess of phosphine.



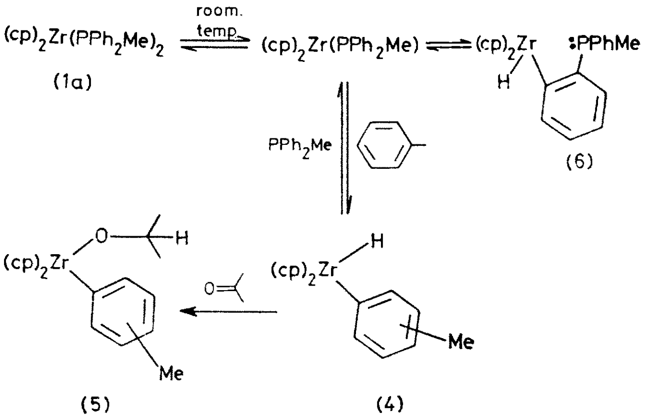
a; L_2 = $2Ph_2PMe$
b; L_2 = 2 $PhPMe_2$
c; L_2 = $Ph_2PCH_2CH_2PPh_2$ (diphos)
d; L_2 = $Me_2PCH_2CH_2PMe_2$ (dmpe)

Scheme 1. Reagents: i, CO (1 atm.), 6·5 h; ii, diphos; iii, hex-3-yne, 5 h; iv, octa-1,7-diene, 5 h, 90%; v, MeX, fast (X = OSO_2F, Cl, or I); vi, Bu^nCl, 1 h.

R = (Cyclohexyl)methyl; all reactions at room temp. For (**1a**), in the presence of 2 equiv. of PPh_2Me. (**1a**) not isolated. Yields were determined by n.m.r. spectroscopy, and, except where noted, were quantitative, based on $(cp)_2Zr(R)H$.

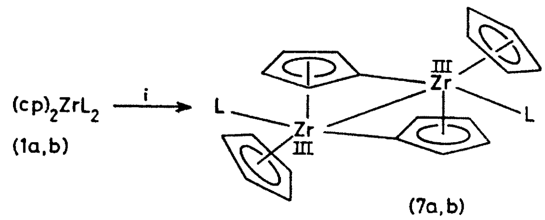
Reactivity patterns for zirconocene bis(phosphine) complexes are shown in Scheme 1. Preliminary rate data indicate that oxidative addition of primary halogenoalkanes proceeds *ca.* 10^3 times faster than does the corresponding oxidative addition to the Rh^I complex reported[4] to be among the most active towards oxidative addition of alkyl halides.[5]

Zirconocene bis(monophosphine) complexes reversibly metallate aromatic solvents under ambient conditions[6] (Scheme 2); these conditions are at least as mild as those so far noted[7] for aromatic solvent metallation by other reactive metal complexes. Although the solvent metallated species (**4**), an arylzirconium hydride, is not directly observable, it can be trapped by reaction with acetone.[3] Accordingly (**1a**) can be converted into (**5**) quantitatively in 3 h (room temperature; 5 equiv. acetone). No product of net metallation of phosphine ligands has been detected;¶ however, it is possible that (**6**) could be too short-lived to be easily trapped because of reductive elimination [back to (**1**)] induced *intramolecularly* by its *ortho*-phosphino group (Scheme 2).



Scheme 2. For compound (**5**) ratio of *m*:*p*, 2:1. No *o*-product was observed.

Oxidative addition of cyclopentadienyl C–H bonds, which deactivates '$(cp)_2Zr$' made by 'traditional' methods, also occurs in thermal decomposition of the zirconocene bis(phosphine) complexes of monomeric phopshines. Complexes (**1a**) and (**1b**) slowly decompose in solution at room temperature over several days, by loss of 1 equiv. of phosphine and 0·5 equiv. of H_2 to give the deep red diamagnetic zirconocene phosphine dimers (**7a,b**) (Scheme 3),** whose structures were assigned on the basis of spectral data. The critical feature of the assignment is the observation of



a; L = Ph_2PMe
b; L = $PhPMe_2$

Scheme 3. i, 50 °C, 1 day, toluene or cyclohexane.

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† Neither triphenylphosphine nor tricyclohexylphosphine partook in this reaction.

‡ When the (α,1-dideuteriomethylenecyclohexyl)zirconium compound was used, α,1-dideuteriomethylcyclohexane was the predominant alkane formed.

§ Satisfactory elemental analyses and mass spectral data have been obtained.

¶ Treating (**1a**) with [$^2H_8$]toluene gives no D-incorporation into the phosphine.

** Prepared using 1 equiv. excess of phosphine; satisfactory elemental analyses were obtained.

the low-field chemical shift for C(1), which shows phosphorus–carbon coupling (J_{P-C} *ca.* 7 Hz), whereas the other carbons of the cp bridge show no observable $^{31}P-^{13}C$ coupling. While n.m.r. data establish the gross structure for (**7**) the relative arrangement of phosphine ligands (*cis*- or *trans*-) cannot yet be ascertained; for (**7b**): ^{1}H (δ C_6D_6): 7·62—7·12 (m, 5H), 6·12 (m, 1H), 5·50 (m, 1H), 5·26 (d, J_{P-H} 1·5 Hz, 5H), 5·24 (m, 1H), 3·97 (m, 1H), 1·46 (d, J_{P-H} 5·2 Hz, 3H), and 1·20 (d, J_{P-H} 5·2 Hz, 3H); $^{31}P\{^{1}H\}$ (δ *vs.* H_3PO_4, C_6D_6): 10·35 p.p.m.; $^{13}C\{^{1}H\}$ (δ C_6D_6, phenyl group signals omitted for clarity); η^5: σ cp: 190·42 (J_{P-C} 7·3 Hz), 111·18, 109·70, 104·92, and 100·90; η^5cp: 99·36; $(CH_3)_2P$: 18·40 (J_{P-C} 15·5 Hz), and 16·35 p.p.m. (J_{P-C} 15·5 Hz). This dimeric structure is analogous to that of niobocene, with which it is isoelectronic.[8] The Zr^{III} dimer (**7b**) is also obtained (in yields of *ca.* 50%) by ligand-induced elimination of H_2 when 'zirconocene' [prepared by autodecomposition of $(cp)_2Zr(R)H$[3] or by Na–Hg reduction of $(cp)_2ZrCl_2$] is treated with (**3b**) at 50 °C in toluene or tetrahydrofuran (THF). These observations suggest that the polymeric zirconocenes prepared by conventional routes may contain bridging hydrides and the η^5:σ-bridging cyclopentadienyl ligand, analogous to niobocene, rather than the bridging fulvalenide ligand found for green stable titanocene[9] (Scheme 3).

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[1] For example, see G. P. Pez, *J. Amer. Chem. Soc.*, 1976, **98**, 8072, and references cited therein.

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[5] Compare with reactivity reported for $(cp)_2Zr(CO)_2$ and $(cp)_2Zr(CO)(PMe_3)$ toward oxidative addition: $(cp)_2Zr(CO)_2$ reacts with MeI in heptane slowly (4 h; 70 °C) to give $(cp)_2Zr(I)Me$ and with diphenylacetylene (4 h; 100 °C) to give the tetraphenylmetallacycle: B. Demerseman, G. Bouquet, and M. Bigorne, *J. Organometallic Chem.*, 1977, **132**, 223.

[6] *cis*- and *trans*-1,2-Dimethylcyclohexane (1 : 1; 60%) were identified (g.l.c.–mass spectroscopy) on hydrolysis. Formation of similar metallacycles from olefins has been noted: R. H. Grubbs and A. Miyashita, *J.C.S. Chem. Comm.*, 1977, 864; S. J. McLain and R. R. Schrock, *J. Amer. Chem. Soc.*, 1978, **100**, 1315; J. McDermott, M. Wilson, and G. M. Whitesides, *ibid.*, 1976, **98**, 6529.

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